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ENERGY-DISPERSIVE, X-RAY REFLECTIVITY DENSITY MEASUREMENTS OF POROUS SiO_2 XEROGELS

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X-ray reflectivity has been used to nondestructively measure the density of thin, porous, SiO_2-based xerogels. Critical angle, defined by total external reflection, was measured for multiple x-ray energies to correct for sample misalignment error in the determination of the density for the films. This density was used to extrapolate the percentage of porosity, assuming a bulk SiO_2 density standard. The results were compared to those obtained by Rutherford backscattering and ellipsometry techniques.

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INTRODUCTION

High speed, small feature size, integrated circuits require low-k dielectrics to isolate interconnect wires without spreading signals or slowing ultimate device speed. Recently low-k materials have been actively pursued by researchers to replace the conventional SiO_2 as interlayer dielectrics (ref 1). For a dielectric constant less than 4 (the dielectric constant of the conventional SiO_2), but larger than 2, there are several material choices. However, there are only two classes of materials that have a dielectric constant less than 2, namely, the Teflon family (ref 2) and porous materials (ref 3). Xerogels are SiO_2-based materials that can exhibit extremely low-k dielectric properties due to high porosity. Characterizing the porosity of the materials is quite a challenging task, particularly because they are in thin-film form.

Ellipsometry is perhaps the most common tool used to measure the index of refraction of dielectric films. The index of refraction of the porous SiO_2 is between 1.46 (for a solid SiO_2 film) and 1 (for air). The density of the porous films—and therefore the porosity—can be determined because it is directly related to the index of refraction. In using this technique, knowledge of the substrate (index of refraction) is required. The technique becomes complicated if the substrate contains a metal diffusion barrier, and/or a thin dielectric liner such as solid SiO_2 (ref 4), necessary to prevent the diffusion of a metal conductor, such as copper, into the dielectric layer.

Another way to determine the density of the porous material is by the Rutherford backscattering spectrometry(RBS) technique (ref 5). This technique provides a depth profile of the elemental composition in the film. Determining the film density from RBS requires knowledge of the film thickness. When a porous film is deposited onto the SiO_2 liner, an analysis can be quite complicated.

In the present work, we explore the use of the x-ray reflectivity technique (ref 6) to determine the xerogel film density and porosity. This technique does not require either knowledge of the substrate properties or thickness of the film. In this technique, the critical angle, defined by the condition for the total external reflection, is measured and correlated to the density of the film.

EXPERIMENTAL METHOD

A Scintag x-ray diffractometer was used to collect the data for the present work. Fine-focus 0.4-mm x 12-mm copper and chromium x-ray tubes were used. A 0.05-mm source divergence slit was used to reduce beam divergence in the plane of reflection to 0.043 degree. Soller slits provided 2.4 degrees beam divergence out of the reflection plane. A 6-mm round collimator provided beam attenuation and enhanced the source image uniformity. On the receiving side, a 0.05-mm slit was placed approximately 1-mm in front of the geometrically focused Peltier-cooled silicon detector. A single-channel analyzer with a 300-eV window provided wavelength selection for the scans. The θ-2θ goniometer allowed independent alignment of the detector axis and the sample axis. The tube height and sample height could also be adjusted with precision to ensure that the source, source slit, sample, receiving slit, and detector were all coaxial.

The reflectivity data were normalized for a geometry-induced intensity variation with angle caused by incident beam width. For a zero-degree incident angle, the x-ray beam illuminates the entire sample with a low intensity, since the majority of the beam width is not focused on illuminating the sample. As the sample is tilted to higher angles, the beam width begins to focus on the center of the sample supplying an apparent increase in intensity with an increase in reflectivity angle. To correct for this intensity change, the measured reflectivity intensity, $I_{measured}$, is normalized to a constant incident intensity, $I_{normalized}$, by $\tan(\theta)$ to adjust for the apparent increase of beam intensity with increase in angle

$$I_{normalized} \cong I_{measured} / \tan(\theta) \qquad (1)$$

RESULTS

Figure 1 shows the normalized reflectivity data as a function of 2θ for Sample #1. The sample was a 0.5-μm xerogel spin-coated and cured film on a silicon wafer. A 0.4-mm × 8-mm copper Kα source with power set at 15 kV and 2 mA was used to take the energy dispersive data set. Specular reflectivity scans were taken at four distinct energies—8.04 keV, 7.00 keV, 5.96 keV, and 5.41 keV—using a nominal 300-eV single-channel analyzer window as follows:

- 8.04-keV reflectivity data were fit to a 0.85 g/cm^3 xerogel density
- 7.00-keV reflectivity data were fit to a 0.80 g/cm^3 xerogel density
- 5.96-keV reflectivity data were fit to a 0.90 g/cm^3 xerogel density
- 5.41-keV reflectivity data were fit to a 0.90 g/cm^3 xerogel density

The position of the first kink in each curve is the critical angle for the porous SiO_2, and the position of the second kink corresponds to that of the silicon substrate underneath the film.

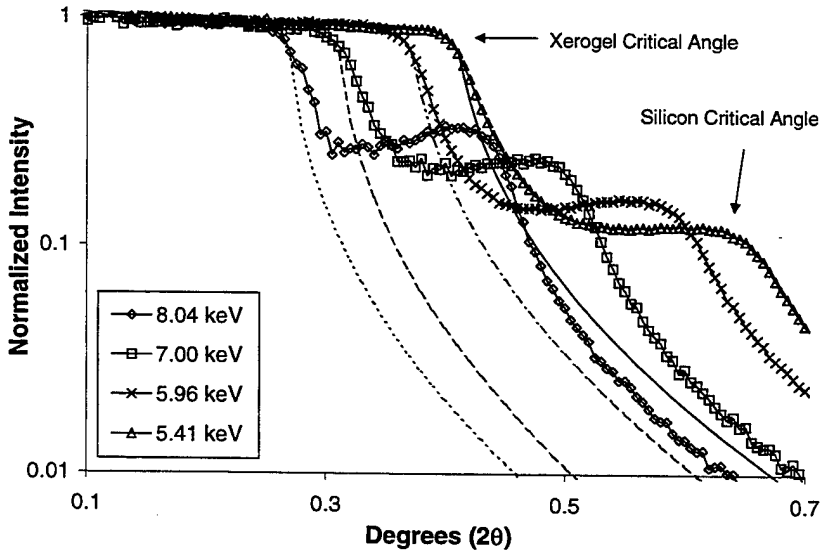

Figure 1. Reflectivity data for misaligned (-0.18°) xerogel Sample #1 showing about 50% porosity for four energies.

From the Fresnel equations, the critical angle, θ_c, of the porous SiO_2 is related to the real component of the index of refraction, δ, by

$$\cos(\theta_c) \cong 1 - \delta \tag{2}$$

Using a simple model of the air/film interface Fresnel reflection, a reflection coefficient can be calculated for a given δ, at each incident angle. This reflection coefficient squared models the behavior of the specular reflectivity data in the region where the total external reflection, the flat region, is replaced by attenuation and penetration. We tried iterative values of δ in the model to obtain the best-fit condition. The dotted curves in Figure 1 are a result of this fit.

For a given film

$$\delta \sim \rho_e \lambda^2 \tag{3}$$

where ρ_e is the number of electrons per volume in the film, and λ is the wavelength of the x-ray (ref 6). The film mass density, ρ, can therefore be obtained through ρ_e. The Sample #1 curve in Figure 2 is a plot of the extracted porous film density as a function of the wavelength for a misaligned sample. Ideally, the value of the film density extracted from different x-ray energies should be the same. However, sample misalignment and beam misalignment in x-ray reflectivity measurement can cause an incorrect index of refraction and density calculation. This problem is amplified for higher energy scans, since the grazing angles used are much smaller. This error is linear with energy and allows an extrapolation of the true density ("zero energy density") by linear fitting the results from several x-ray energies (ref 7).

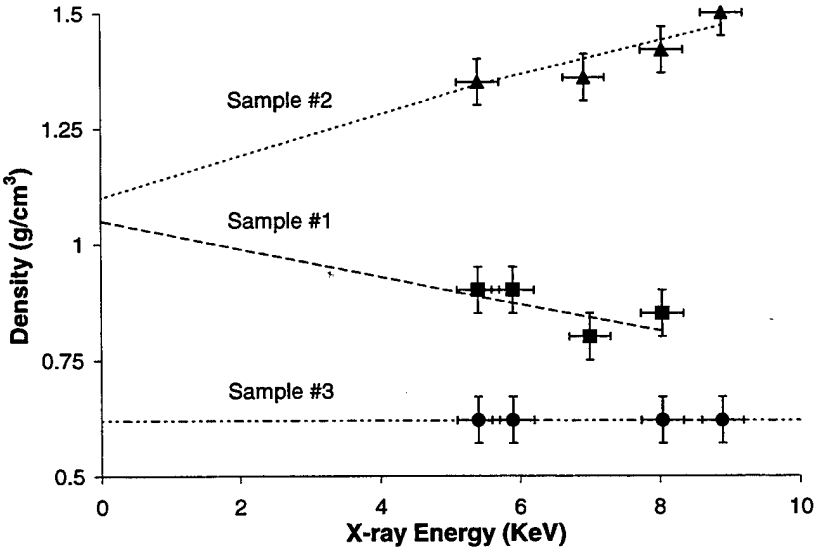

Figure 2. Reflectivity-derived density versus energy for xerogel samples.

In the present case, Sample #1 had a -0.018 degree misalignment with respect to the exact specular direction. (The negative sign indicates that the misalignment was such that the incident angle was less than the reflected angle.) The extrapolation of the linear fit gave a density of 1.05 g/cm^3 (instead of 0.85 g/cm^3 measured at 8.04 keV) at zero energy. This density gave a porosity of about 50%.

To further illustrate the misalignment issue, we performed the reflectivity measurements on Sample #2 with a +0.024 degree misalignment. This sample was cut from the same wafer as Sample #1, and therefore had the same film density. The Sample #2 curve in Figure 2 shows that the density obtained at the range of energies used—8.9 keV, 8.04 keV, 7.00 keV, and 5.41 keV—was somewhat higher than the true value of 1.10 g/cm^3. However, the extrapolated value (to the zero keV axis) was about the same as the extrapolated value from the Sample #1 curve.

Sample #3 had a different porosity. For this sample, a copper Kα, 0.4-mm × 8-mm source with power set at 40 kV and 2 mA was used to take the energy dispersive data. Specular reflectivity scans were again taken at four distinct energies. With the higher set power, a round, 2-mm collimator was added to the beam path to reduce intensity and illuminate a smaller sample area. The data were again normalized and fit to give a density of about 0.65 g/cm^3, which corresponded to a porosity of about 70%. The Sample #3 curve in Figure 2 depicts an excellent alignment in that the all-measured density from different energies gave about the same value.

Table 1 compares densities obtained from the three measurement techniques, x-ray reflectivity, RBS, and ellipsometry. Although the overall values obtained by different techniques were reasonably close, some discrepancies can be seen. One should keep in mind that the x-ray reflectivity technique measures the film density near the surface region, while RBS and ellipsometry techniques measure the average density of the whole film. All density determination methods discussed here assume that a nonporous region in the xerogel film has a density similar to the bulk SiO_2. This assumption may not be rigorously accurate (ref 8).

Table 1. Density of Xerogels Measured by Multiple Techniques

METHOD	Sample #1		Sample #2		Sample #3	
	g/cm^3	Porosity	g/cm^3	Porosity	g/cm^3	Porosity
X-Ray Reflectivity	1.11 ±0.1	49 ±5%	1.05 ±0.1	52 ±5%	0.65 ±0.05	70 ±2%
RBS	1.21 ±0.1	45 ±5%	1.21 ±0.2	45 ±5%	0.65 ±0.20	70 ±5%
Ellispometry	1.16 ±0.1	47 ±5%	1.24 ±0.1	43 ±5%	0.55 ±0.10	75 ±5%

Nevertheless, the x-ray energy dispersive reflectivity method provides a complementary way to determine the density of porous films. This method does not require the knowledge of the substrate or the thickness of the films. Therefore, the method can be applied to films deposited on a metal barrier layer or a dielectric liner. The method is suitable for in-line characterization during semiconductor processing.

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